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(21) International Application Number: PCT/FI97/00353 (22) International Filing Date: 6 June 1997 (06.06.97) (30) Priority Data: 962366 7 June 1996 (07.06.96) FI (71) Applicant (for all designated States except US): BOREALIS POLYMERS OY [FI/FI]; P.O. Box 330, FIN-06101 Porvoo (FI). (72) Inventors; and (75) Inventors/Applicants (for US only): HAGSTRÖM, Bengt [SE/SE]; Tvetgatan 153, S-442 33 Kungälv (SE). SAHILA, Aimo [FI/FI]; Tursontie 4 B 7, FIN-04200 Kerava (FI). ÄÄRILÄ, Jari [FI/FI]; Partiomiehentie 1 B 31, FIN-06100 Porvoo (FI). (74) Agent: BERGGREN OY AB; P.O. Box 16, FIN-00101 Helsinki (FI).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: ETHYLENE POLYMER PRODUCT HAVING A BROAD MOLECULAR WEIGHT DISTRIBUTION, ITS PREPARATION AND USE (57) Abstract Although ethylene polymer products having a bimodal or multimodal molecular weight distribution have good processability and mechanical properties, these properties are not entirely satisfactory. Such bimodal or multimodal ethylene polymer products are now being improved by (a) forming a blend of a first ethylene polymer having a first average molecular weight and a first molecular weight distribution and at least a second ethylene polymer having a second average molecular weight which is higher than said first average molecular weight and a second molecular weight distribution giving the blend a third average molecular weight and a third molecular weight distribution which is at least bimodal, (b) heating and melt processing the blend of step (a) into a molten ethylene polymer having a fourth average molecular weight and a fourth molecular weight distribution, and (c) cooling and solidifying the molten ethylene polymer into said ethylene polymer product, whereby in step (b), the blend of step (a) is subjected to controlled free radical reactions in such a way that the fourth average molecular weight is higher than, or approximately equal to, the third average molecular weight, and the fourth molecular weight distribution is broader than the third at least bimodal molecular weight distribution.		

ETHYLENE POLYMER PRODUCT HAVING A BROAD MOLECULAR WEIGHT DISTRIBUTION, ITS PREPARATION AND USE

- 5 The invention relates to a process for the preparation of a solid ethylene polymer product, containing from 0.0 to 20% by weight of repeating units of a C₃-C₁₀ α -olefin and having a broad molecular weight distribution.

10 In certain applications, where films, bottles, cables and pipes are produced by extrusion or blow molding, the ethylene polymers having narrow molecular weight distribution are not satisfactory, because of the poor melt flow properties and poor processability. Therefore, different approaches have been suggested for manufacturing polyethylenes having a broad molecular weight distribution. One approach to widen the molecular weight distribution is to blend a low molecular weight ethylene polymer with a high molecular weight ethylene polymer either mechanically or
15 in solution. More than two ethylene polymers having different molecular weights can also be mixed together.

20 Attempts have been made to broaden molecular weight distribution by a proper selection of catalysts.

There are also known various multi-stage processes for broadening the molecular weight distribution by carrying out the polymerization using different hydrogen and co-monomer concentrations in each stage.

25 US 5,326,835 discloses a multi-stage process for producing ethylene polymer having a bimodal and/or broad molecular weight distribution in a multi-step reaction sequence. According to this patent, the first reaction step is performed in a loop reactor and one or more subsequent steps are performed in one or more gas phase
30 reactors. The molecular weight distribution can be controlled by using different concentrations of hydrogen chain transfer agent and co-monomer in different steps.

By bimodal and multimodal distribution is generally and in connection with the present invention meant a broad molecular weight distribution produced by blending
35 two or more polymer components with different molecular weights or by polymerizing to different molecular weights in a process with two or more reactors in series. Unimodal distribution is obtained with essentially only one molecular weight fraction.

third average molecular weight and a third molecular weight distribution which is at least bimodal;

(b) the blend of step (a) is heated and melt processed into a molten ethylene polymer having a fourth average molecular weight and fourth molecular weight distribution;

a stabilizer is optionally added in step (b), and

(c) the molten ethylene polymer is cooled and solidified into said ethylene polymer product.

The process according to the invention is substantially characterized in that in the above step (b), the blend of step (a) is subjected to controlled free radical reactions so that the fourth average molecular weight is higher than, or approximately equal to, the third average molecular weight, and the fourth molecular weight distribution is broader than the third at least bimodal molecular weight distribution.

The average molecular weights and the molecular weight distributions can be measured and expressed by any conventional method applied to ethylene polymers products. In this connection, it is convenient that the average molecular weights are measured and expressed as melt flow rates MFR^i_m , where i refers to the first, second, third and fourth average molecular weight and m refers to the load of the piston used for measuring the MFRs, which load in the following examples generally is 5.0 kg (ISO 1133), the molecular weight distributions are expressed as the flow rate ratios, $FRR^i_{m^1/m^2}$, i.e. the ratios between high load MFR^i s and low load MFR^i s, where i refers to the first, second, third and fourth molecular weight distribution, and m^1 and m^2 refer to the high load, generally 21.6 kg, and low load, generally 5.0 kg or 2.16 kg, respectively.

By Melt Flow Rate (MFR) is meant the weight of a polymer pressed through a standard cylindrical die at a standard temperature in a laboratory rheometer carrying a standard piston and load. Thus MFR is a measure of the melt viscosity of a polymer and hence also of its molecular weight. The smaller the MFR, the larger is the molecular weight. It is frequently used for characterizing a polyolefin, especially polyethylene, when the standard conditions MFR_m are: temperature 190°C; die dimensions 9.00 cm in length and 2.095 cm in diameter; load of the piston, 2.16 kg ($m=2$), 5.0 kg ($m=5$), 10.0 kg ($m=10$), 21.6 kg ($m=21$). See Alger, M.S.M., Polymer Science Dictionary, Elsevier 1990, p. 257.

led to a narrowing of the molecular weight distribution and the oxygenation of polyethylene did not influence it. The upper limit of the disclosed flow rate ratios are not to be interpreted as limiting the scope of protection, but is only based on the embodiment of the examples.

5

The most important feature of the heating and melt processing step (b) is the occurrence of controlled free radical reactions. Free radical reactions can be effected in many ways. Firstly, free radicals may be generated from initiators in diverse ways, among which thermal or photochemical intermolecular bond cleavage, redox reactions, and photochemical hydrogen abstraction are the most common, but other processes such as the use of γ -radiation or electron beams find application. Free radicals can also be generated by means of reaction of the ethylene polymer blend by means of thermal decomposition with or without the presence of oxygen. Thermal treatment is a suitable method, especially if unstabilized polyethylene is used or if the used ethylene polymer is destabilized during the treatment.

15

Among decomposable thermal initiators, the following can be mentioned: azo-compounds such as azobisisobutyronitrile (AIBN), peroxy compound such as diacyl peroxides, acetyl alkylsulfonyl peroxides, dialkyl peroxydicarbonates, *tert*-alkyl-peroxyesters, *OO-tert*-alkyl *O*-alkyl monoperoxycarbonates, di(*tert*-alkylperoxy)-ketals, di(*tert*-alkyl)peroxides, *tert*-alkyl hydroperoxides, and ketone peroxides, redox initiators, etc. According to one embodiment of the invention, the half life of the thermal initiators used during 10 h is from 38 to 172°C, preferentially from 54 to 128°C.

25

Especially preferential are peroxy compounds of which the following can be mentioned: diacylperoxides, such as dibenzoyl peroxide BPO, di(2,4-dichlorobenzoyl) peroxide, diacetyl peroxide, dilauroyl peroxide, didecanoyl peroxide, diisononanoyl peroxide and succinic acid peroxide; commercial peroxy esters, such as di-*tert*-butyl diperoxyphthalate, *tert*-butyl perbenzoate, *tert*-butyl peracetate, *tert*-amyl perbenzoate, 2,5-di(benzoylperoxy)-2,5-dimethylhexane, *tert*-butyl peroxy-maleic acid, *tert*-butyl peroxyisobutyrate, *tert*-butyl peroxy-2-ethylhexanoate(*tert*-butyl peroctoate), *tert*-amyl peroctoate, 2,5-di(2-ethylhexanoylperoxy)-2,5-dimethylhexane, *tert*-butyl peroxy-pivalate, *tert*-amyl peroxy-pivalate, *tert*-butyl peroxyneodecanoate, *tert*-amyl peroxyneodecanoate, α -cumyl peroxyneodecanoate; diperoxyketals, such as ethyl-3,3-di(*tert*-butylperoxy)butyrate, ethyl 3,3-di(*tert*-amylperoxy)butyrate, *n*-butyl 4,4,-di(*tert*-butylperoxy)valerate, 2,2-di(*tert*-butylperoxy)butane, 1,1-di(*tert*-butylperoxy)cyclohexane, 1,1-di(*tert*-butylperoxy)-3,3,5-trimethylcyclo-

35

The amount of generated radicals is, naturally also dependent on the amount of initiators added to step (b) of the claimed process. In step (b) the preferential initial content of initiator or optionally content of initiator left after reaction with an added stabilizer, is from 20 ppm to 2000 ppm, most preferentially from 50 ppm to 500 ppm, calculated on the weight of the blend of step (a). Later in step (b), of course, the content of initiator decreases as it decomposes into radicals.

As was mentioned above, the average heating and melt processing time in step (b) of the claimed process has much influence on the generation of free radicals. Depending on the other parameters used, it can vary very much. When using radical initiators, the average heating and melt processing time in step (b) is preferentially from 0.1 min to 30 min and most preferentially from 0.5 min to 10 min.

In the embodiment disclosed above, the blend of step (a) is subjected to free radical reactions by means of free radical initiators. However, there is a second very suitable process for inducing radical reactions. Radical reactions can namely be induced merely by heating the polymer during step (b). In such a step of thermal treatment, the temperature is preferentially from 220°C to 320°C, most preferentially from 240°C to 300°C. In such a case, the average heating and melt processing time in step (b) is from 0.1 min to 30 min, preferentially from 0.5 min to 10 min.

When generating radicals by means of thermal treatment, it is preferable to use an essentially unstabilized or lightly stabilized blend of step (a) as raw material for step (b) of the claimed process.

In order to stabilize the final ethylene polymer product, a stabilizer can be added at the end of step (b), after the needed amount of radical reactions have taken place. It is then added to and mixed with the molten ethylene polymer.

In the following, stabilizers for controlled radical treatment and/or final stabilization are disclosed. All polymeric materials undergo oxidation which can occur in every stage of the life cycle of the polymer (processing, storage, end-use (ageing, weathering)). The reaction is initiated by heat, light, mechanical stress (shear), catalyst residues, impurities etc. and yields alkyl radicals (R·). The generated free radicals can lead to a degradation of the polymer:

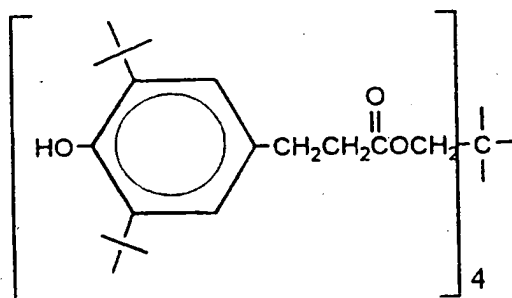
The main antioxidants for polyolefins are often referred to the Ciba-Geigy's Irganox and Irgafos trademarks (also by their competitors). The chemical structures of the antioxidants are viewed in the Table below.

5 Table

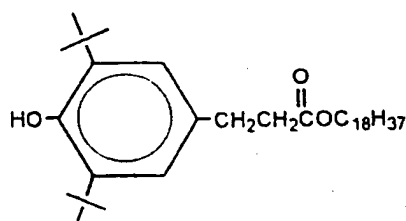
Antioxidants for polyolefins: chemical structures

Sterically hindered phenols:

Irganox 1010

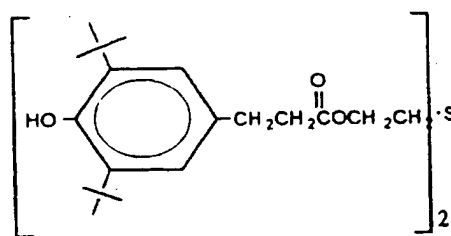


Irganox 1076



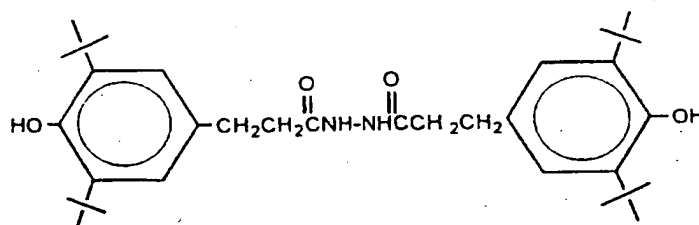
10

Irganox 1035



Metal deactivator

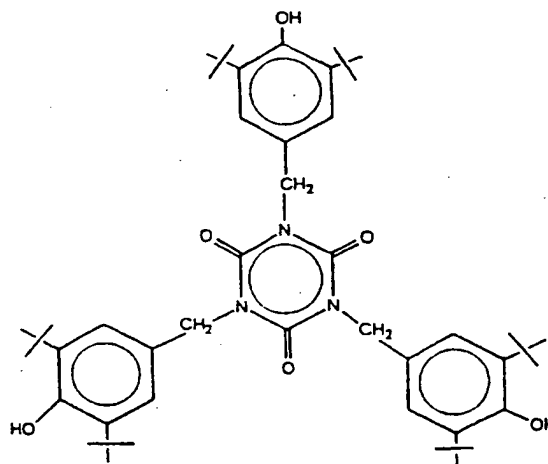
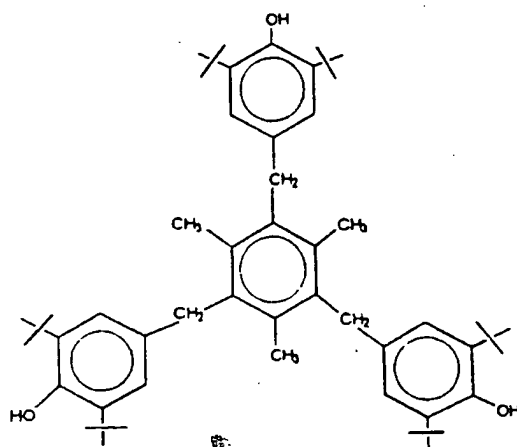
Irganox MD 1024



Irganox 1330

Irganox 3114

15



The free-radical scavengers inhibit the propagation through a combination of scavenging and terminating free radicals and decomposing hydroperoxides to harmless products. The hindered amine light stabilizers (HALS) belong to this group of UV stabilizers.

5

More specifically, it is dependently of the antioxidant fed, preferential in step (b) to add from 0 to 500 ppm of a first stabilizer to the blend of step (a) essentially at the beginning of step (b) and to add from 400 to 1400 ppm of a second stabilizer to the molten ethylene polymer essentially at the end of step (b), the first and second stabilizers being equal or different. According to a preferred embodiment of adding stabilizers, the first stabilizer added in step (b) is a different stabilizer than the second stabilizer, most preferentially so, that the first stabilizer is a weak process stabilizer allowing radical reactions partially, whereas the second stabilizer is a strong process stabilizer essentially preventing radical reactions during melt processing.

15

As was indicated in the introduction, the bimodal raw material of the heating, melt processing and controlled free radical treatment of step (b) of the claimed process can be produced by essentially two main process steps, namely the mixing of at least two ethylene polymers having different average molecular weights and by polymerizing in a process having at least two internal steps leading to different molecular weights. If necessary, the two methods can be combined in any suitable way to give the right molecular weight distribution for step (b).

20

In the following, the mixing in step (a) of a first ethylene polymer and at least a second ethylene polymer is analyzed more closely.

25

The mixing can be a mechanical mixing of two or more granulates, but is preferentially a melt mixing.

30

The mixing of step (a) is preferentially a mixing of two molten polymers e.g. by melt processing and compounding equipment such as an extruder.

When feeding the first ethylene polymer to the mixing step (a), the melt flow ratio MFR^{12} of the first ethylene polymer is from 50 to 2000 g/10 min, most preferentially from 100 to 1500 g/10 min. When feeding the second, and optionally the third, etc., polymer to the mixing step (a), their melt flow ratio $MFR^{2,etc.21}$ is preferentially from 0.05 to 50 g/10 min. most preferentially from 0.10 to 20/10 min.

35

molecular weight ethylene polymer is prepared by polymerizing in a substep (a₂), and optional further ethylene polymers are prepared by polymerizing in optional further substeps, whereby the ethylene polymer of each step is present in the following step.

5

The polymerization conditions of each substep are such, that ethylene polymers are produced the average molecular weight of which differs so that the end product is bimodal or multimodal. Typically in substep (a₁), a temperature of 40°C to 120°C is used, and, independently, in substep (a₂), a temperature of 60°C to 140°C is used.

10

The polymerizations are typically insertion polymerizations where Ziegler-Natta or single site polymerization catalyst systems are used. For example in substep (a₁) and/or (a₂), a catalyst system is typically used, which is based on at least a tetravalent titanium compound as procatalyst and an organoaluminum compound as cocatalyst. When Ziegler-Natta catalyst system are used, procatalyst is preferentially based on titanium tetrachloride TiCl₄, magnesium chloride MgCl₂, and an optional inert carrier and/or an optional electron donor compound, and a typical cocatalyst is a trialkylaluminum compound. Typical catalysts are e.g. prepared according to WO 91/12182 and WO 95/35323 which are herewith included by reference. A preferential single site polymerization catalyst system is that based on a group 4 (IUPAC 1990) metal metallocene an alumoxane.

15

20

When performing a polymerization in step (a), substeps (a₁) and (a₂) can be performed in any order, preferentially so that the catalyst system added to one substep catalyst system is also used in the next and other optional additional substeps.

25

The most convenient way to regulate the molecular weight during polymerization is to use hydrogen, which acts as a chain-transfer agent by intervening in the insertion step of the polymerization mechanism. Thus it is preferential that in substep (a₁) a hydrogen amount is used, leading to a melt index MFR₁₂ of the first ethylene polymer of from 50 to 2000 g/10 min., most preferentially from 100 to 1500 g/10 min., when substep (a₁) is performed first.

30

35

The properties of the first, second etc. ethylene polymers forming the blend of step (a) also depend on the use of minor amounts of an α -olefin, which is not ethylene. Typically, in substep (a₁), no or a small amount of C₃-C₁₀ α -olefin is used, so that the first ethylene polymer has a C₃-C₁₀ α -olefin repeating unit content of 0.0 to

then based on radical reactions. The reactions can be initiated by peroxides or by using heat and no or a reduced amount of stabilizers in the extruder. The absence or reduced amounts of stabilizers make the controlled peroxide reactions possible in the compounding machine. The tailoring reactions increase the amount of high Mw
5 molecules, which can be seen in the increased zero shear rate viscosity (lower MFR values).

Tailoring during melt compounding gives following improvements without additional process or processing steps:

10

1. Balanced application properties can be obtained by fine-tuning the tailoring.

2. The elasticity of the ethylene polymer material is increased. This gives better melt strength and processability on film blowing line. Another improvement is a
15 more balanced orientation, which gives better tear strength in the machine direction and thus improves the overall tear strength. Increased elasticity also improves the neck-in and draw down properties on different extrusion applications and gives better stability for the broadness of film on cast-line, pipe coating, extrusion coating etc.

20

3. The weight swell is an important parameter on blow molding lines. By weight swell is meant the weight of a blow article compared to a reference, using constant parrison length. To have easy processability it has to be adjusted to a suitable level. Tailoring gives a possibility to fine-tune, when necessary, the flow properties and
25 weight swell, which is a function of die swell and sagging. Tailoring decreases die swell and on the other hand the low zero shear rate viscosity obtained results in less sagging and also slower rate of swelling.

In the following, examples are disclosed to illustrate the invention.

30

EXAMPLES

All the examples are made with materials produced in two or more reactors connected in series.

35

Example 1

Bimodal polyethylene (A) was polymerized with Ziegler-Natta type catalyst prepared according to WO 95/35323 in one loop and one gas phase reactor which are

Example 2

Controlled swell and flow properties (rheology) by tailoring.

5 Bimodal polyethene (B) was polymerized with Ziegler-Natta type catalyst prepared according to WO 95/35323 in one loop and one gas phase reactor which are operated in series. Ethene was polymerized in presence of hydrogen in the loop resulting in $MFR_2 = 363$. Ethene was polymerized with 1-butene and hydrogen in the gas phase reactor. The production rate split of reactors was 45% / 55%. The final product $MFR_{21} = 30$ and density 957 kg/m^3 . The polymerization results are
10 presented in Table 1.

The powder from the above polymerization was compounded on Werner & Pfleiderer ZSK-30 extruder without and with peroxide addition. The peroxide was bis(tert.butylperoxyisopropyl)benzene (Perkadox 14S) and it was added as a master
15 batch in the same powder. The master batch was made in a Pappenmeyer mixer. The compounding conditions were 200 rpm, 7 kg/h and $T_m = 210^\circ\text{C}$.

The samples were tested by measuring MFR (by using standard ISO 1133), rheology and on Battenfeldt Fischer VK 1-4 blow molding line having screw diameter 50 mm and length 20 D by blowing 0.5 liter bottles. Rheometrics RDA II
20 dynamic rheometer was used for rheological characterization. Measurements were made under nitrogen atmosphere at 190°C . In this way storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) were obtained as a function of complex modulus (G^*). Shear thinning index $SHI_{x/y}$ was defined as the ratio of complex viscosities at a low G^* value of x and at high G^* value of y.

25

$$SHI_{x/y} = \eta(x \text{ kPa}) / \eta(y \text{ kPa})$$

The shear thinning index (SHI) measured at low shear and at high shear is used to describe the broadness of molecular weight distribution. The larger the SHI, the
30 broader is the distribution.

The example shows the possibility to adjust the processability of bimodal polyolefin material on blow molding lines by molecular weight tailoring. The weight swell is an important parameter on blow molding lines. To have easy processability it has to
35 be adjusted to a suitably low level. Tailoring gives a possibility to fine-tune, when necessary, the flow properties and weight swell, which is a function of die swell and

rate split of loop and gas phase reactors was 42% / 58%. The final product MFR₂₁ = 6.8 and density 945 kg/m³.

Above described polymer was tailored during the melt homogenization step on Werner&Pfleiderer ZSK-70 twin screw extruder by feeding different amounts of Irganox B561 stabilizer with powder into the extruder and additionally by feeding 500 ppm Uvinul 2003 stabilizer into the latter part of the extruder. The feeding point of Uvinul was 14 * screw distance from the polymer feeding point. The total screw length of the extruder was 20 * screw diameter. Reference material was run without Uvinul 2003 feed. The compounding conditions were screw speed 250 rpm, T_m=275°C and output 260 kg/h.

The test materials were film blowed on Alpine film blowing line having 65 mm screw diameter. The used blow up ratio was 3.5. The neck height was 8 * die diameter and film thickness was 15 µm.

The example clearly shows improved bubble stability during film blowing and more balanced orientation which can be seen as better balance between machine direction (MD) and transverse direction tear strength (TD) for the film. The results are presented in Table 4.

Table 4

	Test #1	Test #2	Test #3	Reference
Irganox B561 feed	0 ppm	400 ppm	700 ppm	1500 ppm, w/o Uvinul
BUR _{eff} *	5.3	4.2	3.5	3.4
Bubble stability	excellent	excellent	some instability	fair
Dart drop ****	70 g	280 g	280 g	248
Tear strength (MD/TD)**	20/13 mN/µm	20/33 mN/µm	16/67 mN/µm	7/148

*) BUR_{eff} = Diameter of the bubble / Diameter of contracted neck

**) MD = machine direction, TD = transversal direction. Method = ISO 6383/2

***) Dart drop, ISO 7765-1

Example 4

Bimodal polyethylene (D) was polymerized with said Ziegler-Natta type catalyst in one loop and one gas phase reactor which are operated in series. Ethene was

Example 5

Bimodal polyethene (E) was polymerized with said Ziegler-Natta type catalyst in one loop and one gas phase reactor which are operated in series. The catalyst was prepolymerized before feeding into the loop reactor. The prepolymerization degree was 100 g/g. Ethene was polymerized in presence of hydrogen and 1-butene in the loop reactor resulting in $MFR_2 = 540$ and density 950 kg/m^3 . Ethene was polymerized with 1-butene and hydrogen in the gas phase reactor. The production rate split of loop and gas phase reactors was 43% / 57%. The final product $MFR_{21} = 25$ and density 922 kg/m^3 .

10

Above described polymer was tailored during the melt homogenization step on Werner&Pfleiderer ZSK-70 twin screw extruder by feeding 500 ppm Irganox B225 stabilizer with powder into the extruder and additionally by feeding 500 ppm or 900 ppm Ronotec CF-120 stabilizer into the latter part of the extruder. The feeding point of Ronotec was 14 * screw distance from the polymer feeding point. The total screw length of the extruder was 20 * screw diameter. Reference material was run without Ronotec CF 120 feed.

20

The test materials were film blowed on Reitenhauser film blowing line having 150 mm die diameter. The used blow up ratio was 3. The neck height was 8 * die diameter and film thickness was 25 μm .

25

The example clearly shows improved bubble stability during film blowing. The results are presented in Table 6.

Table 6

Ronotec	500 ppm	900 ppm	-
	Test #1	Test #2	Test #3 reference
Irganox B 225 feed	500 ppm	900 ppm	2500 ppm
BUR _{eff} *	3.8	3.5	2.7
Bubble stability	excellent	excellent	some instability

*) $BUR_{eff} = \text{Diameter of the bubble} / \text{Diameter of contracted neck}$

Claims

1. Process for the preparation of an ethylene polymer product, containing from 0.0 to 20% by weight of repeating units of a C_3-C_{10} α -olefin and having a broad molecular weight distribution, in which process:
 - 5 (a) a first ethylene polymer having a first average molecular weight and a first molecular weight distribution and at least a second ethylene polymer having a second average molecular weight which is higher than said first average molecular weight, and a second molecular weight distribution are formed into a blend having a third average molecular weight and a third molecular weight distribution which is at least bimodal;
 - 10 (b) the blend of step (a) is heated and melt processed into a molten ethylene polymer having a fourth average molecular weight and fourth molecular weight distribution; a stabilizer is optionally added in step (b), and
 - 15 (c) the molten ethylene polymer is cooled and solidified into said ethylene polymer product, characterized in that in step (b), the blend of step (a) is subjected to controlled free radical reactions so that the fourth average molecular weight is higher than, or approximately equal to, the third average molecular weight and the fourth molecular weight distribution is broader than the third at least bimodal molecular weight distribution.
 - 20
2. Process according to claim 1, characterized in that the average molecular weights are measured and expressed as melt flow rates MFR^i_m , where i refers to said first, second, third and fourth average molecular weight, and m refers to the load of the piston used for measuring the MFRs, which load preferentially is 5.0 kg (m=5) (ISO 1133), the molecular weight distributions are expressed as the flow rate ratios, $FRR^i_{m^1/m^2}$, i.e. the ratios between high load MFR's and low load MFR's, where i refers to the first, second, third and fourth molecular weight distribution and m¹ and m² refer to the high load, preferentially 21.6 kg (subindex 21), and low load, preferentially 5.0 kg (subindex 5) or 2.16 kg, respectively.
3. Process according to claim 1 or 2, characterized in that in step (b), the blend of step (a) is subjected to free radical reactions so that the relative MFR_{5.0} decrease, $-(MFR^4_5 - MFR^3_5):MFR^3_5$, is from 5 to 100%, preferentially from 10 to 80%.
- 35

10. Process according to one of claims 6 to 9, characterized in that in step (b), the average heating and melt processing time is from 0.5 min. to 30 min., preferentially from 0.5 min. to 10 min.
- 5 11. Process according to claim 5, characterized in that in step (b), the blend of step (a) is subjected to free radical reactions by means of thermal treatment.
12. Process according to claim 11, characterized in that in step (b), the temperature is from 220°C to 320°C, preferentially from 240°C to 300°C.
- 10 13. Process according to claim 11 or 12, characterized in that in step (b), the average heating and melt processing time is from 0.1 min. to 30 min., preferentially from 0.5 min. to 10 min.
- 15 14. Process according to one of claims 5 to 13, characterized in that in step (b), an essentially unstabilized or slightly stabilized blend of step (a) is used, whereby preferentially at the end of step (b), after the radical reactions have taken place, a stabilizing amount of stabilizer is added to the molten ethylene polymer.
- 20 15. Process according to one of claims 11 to 14, characterized in that in step (b), from 0 to 500 ppm of a first stabilizer is added to the blend of step (a) essentially at the beginning of step (b), and from 400 to 1400 ppm of a second stabilizer is added to the molten ethylene polymer essentially at the end of step (b), the first and second stabilizers being equal or different.
- 25 16. Process according to claim 15, characterized in that in step (b), the first stabilizer is a different stabilizer than the second stabilizer, preferentially so that the first stabilizer is a weak process stabilizer allowing radical reactions partially, whereas the second stabilizer is a strong process stabilizer essentially preventing
- 30 radical reactions during melt processing.
17. Process according to any preceding claim, characterized in that in step (a), the blend is formed by mixing the first ethylene polymer and at least the second ethylene polymer.
- 35 18. Process according to claim 17, characterized in that in step (a), the ratio between the first ethylene polymer and the second ethylene polymer is between 20:80 and 80:20, preferentially between 20:80 and 60:40.

carrier and/or an optional electron donor compound as procatalyst, as well as a trialkylaluminium as a cocatalyst, is used.

26. Process according to claim 24 or 25, characterized in that the catalyst system is added to the first substep (a₁) and the same catalyst system is used in the second and optional additional substeps.
27. Process according to any of claims 24 to 26, characterized in that in substep (a₁), a hydrogen amount is used, leading to a melt index MFR¹₂₁ of the first ethylene polymer of from 50 to 2000 g/10 min., preferentially from 200 to 1500 g/10 min., if substep (a₁) is performed first.
28. Process according to any of claims 24 to 27, characterized in that in substep (a₁), no or little C₃-C₁₀ α-olefin is used so that the first ethylene polymer has a C₃-C₁₀ α-olefin repeating unit content of 0.0 to 10.0% by weight, of the first ethylene polymer.
29. Process according to any of claims 24 to 28, characterized in that in substep (a₂) and further optional substeps, so much C₃-C₁₀ α-olefin is used that at least the second ethylene polymer has a C₃-C₁₀ α-olefin, preferentially 1-butene or 1-hexene, repeating unit content of from 1.0 to 25% by weight, preferentially from 2.0 to 15.0% by weight, of at least the second ethylene polymer.
30. Process according to any of claims 24 to 29, characterized in that in step (a), the ratio between the first ethylene polymer and the second ethylene polymer is between 20:80 and 80:20, preferentially between 20:80 and 60:40.
31. Process according to any of claims 24 to 30, characterized in that in substeps (a₁) and (a₂), said reaction temperature, catalyst system, portions of C₃-C₁₀ α-olefin, amount of hydrogen, and ratio between the first olefin polymer and the second olefin polymer produced, are regulated so that the MFR³₂₁ of the blend of step (a) is between 5 and 50 g/10 min., the C₃-C₁₀ α-olefin repeating unit content of the blend of step (a) is from 0.2 to 20% by weight, preferentially from 0.5 to 15.0% by weight, and the FRR³_{21/5} is between 10 and 40, preferentially so, that after step (b), the fourth molecular weight distribution is at least bimodal.
32. Ethylene polymer product, preferentially a film product, containing from 0.0 to 20% by weight of repeating units of a C₃-C₁₀ α-olefin and having a broad

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 97/00353

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08L 23/04, C08F 10/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08F, C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, WPI, CA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	File WPI, Derwent accession no. 94-086089, MITSUBISHI PETROCHEMICAL CO LTD: "Polyethylenec resin compsn. prodn., for high speed inflation - by kneading compsn. contg. low and high mol. wt. polyethylene"; & JP,A,6009788, 940118, abstract --	1,5-8,17, 32-33
X	EP 0404552 A2 (MOBIL OIL CORPORATION), 27 December 1990 (27.12.90), abstract; page 4, lines 30-35; claims 1-8 --	1,5-8,17, 32-33
X	US 5405917 A (FRANCIS X. MUELLER, JR. ET AL), 11 April 1995 (11.04.95), abstract; claims 1-3, 16; column 4, lines 46-50 --	1,5-9,32-33

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

9 Sept. 1997

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT
Information on patent family members

06/08/97

International application No.
PCT/FI 97/00353

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0404552 A2	27/12/90	CA 2019164 A	21/12/90
		JP 3074447 A	29/03/91
		US 5073598 A	17/12/91
<hr/>			
US 5405917 A	11/04/95	NONE	
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